FINAL REPORT

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INTERCHANGE FOR JOINT RESEARCH ENTITLED:

MINIATURE LASER SPECTROMETER FOR STABLE ISOTOPE MEASUREMENTS

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As a first step in successfully measuring carbon isotopes optically we have previously demonstrated the measurement of $^{13}C/^{12}C$ to a precision of 0.1% using a tunable diode laser and CO_2 spectral lines in the 2300 cm-1 spectral region. This precision of 0.1% (1 per mil) for carbon isotopes is a value sufficiently precise to provide important isotopic data of interest to astrobiologists. The precision presently attainable in gases is sufficient to permit our instrument to be used in the measurement of isotopic ratios of interest to astrobiologists as well as geologists and planetary scientists. See references 1-4.

A small stable isotope laser spectrometer with a 10 cm path gas cell was designed and constructed. The cell was integrated with a liquid nitrogen cooled tunable diode laser and indium antimonide detector for evaluation. Using the small gas cell, preliminary measurements of $^{13}C/^{12}C$ in CO_2 were made employing single-beam sequential acquisitions of the required spectral data. The results indicate an accuracy of 0.1% which is sufficiently high to make meaningful measurements of martian samples. In addition, improvements in the spectrometer gas handling system have been made to markedly reduce $^{13}C/^{12}C$ isotopic fractionation during sample gas cell loading which we expect will lead to further improvements in precision and accuracy.

An important part of making isotopic ratio measurements in solid samples using diode lasers is the conversion of the elements of interest to molecules that have absorption spectra in the mid-ir spectral range accessible by tunable diode lasers. In this project we have investigated the necessary sample preparation procedures to extract carbon, an element of astrobiological importance, from model soil compounds and to convert it to CO_2, a molecule with appropriate optical absorption characteristics for reliable laser spectrometer isotopic ratio measurements of $^{13}C/^{12}C$. We have considered calcium carbonate (5) as a model for a component of the martian regolith, and we have formulated a simple heating protocol for extracting carbon in the form of CO_2.

A pyrolyzer / combustor and gas handling system was designed and assembled with the output coupled to a GC instrument for analysis of pyrolysis products of analog soil samples. Martian soil analogs used included purified sand, organic material (sawdust), and calcium carbonate. Samples and mixtures of samples were pyrolyzed at various temperatures and the pyrolysis product carbon dioxide was detected using the GC. Preliminary results from sawdust (shown in Fig. 1) and from calcium carbonate (shown in Fig. 2) heated in various pressures of oxygen produced CO_2 peaks at 475 and 725 degrees C, respectively, which correspond to CO_2 from organic and inorganic carbon in the samples. Mixtures of purified sand, sawdust, and calcium carbonate produced

FIG. 1

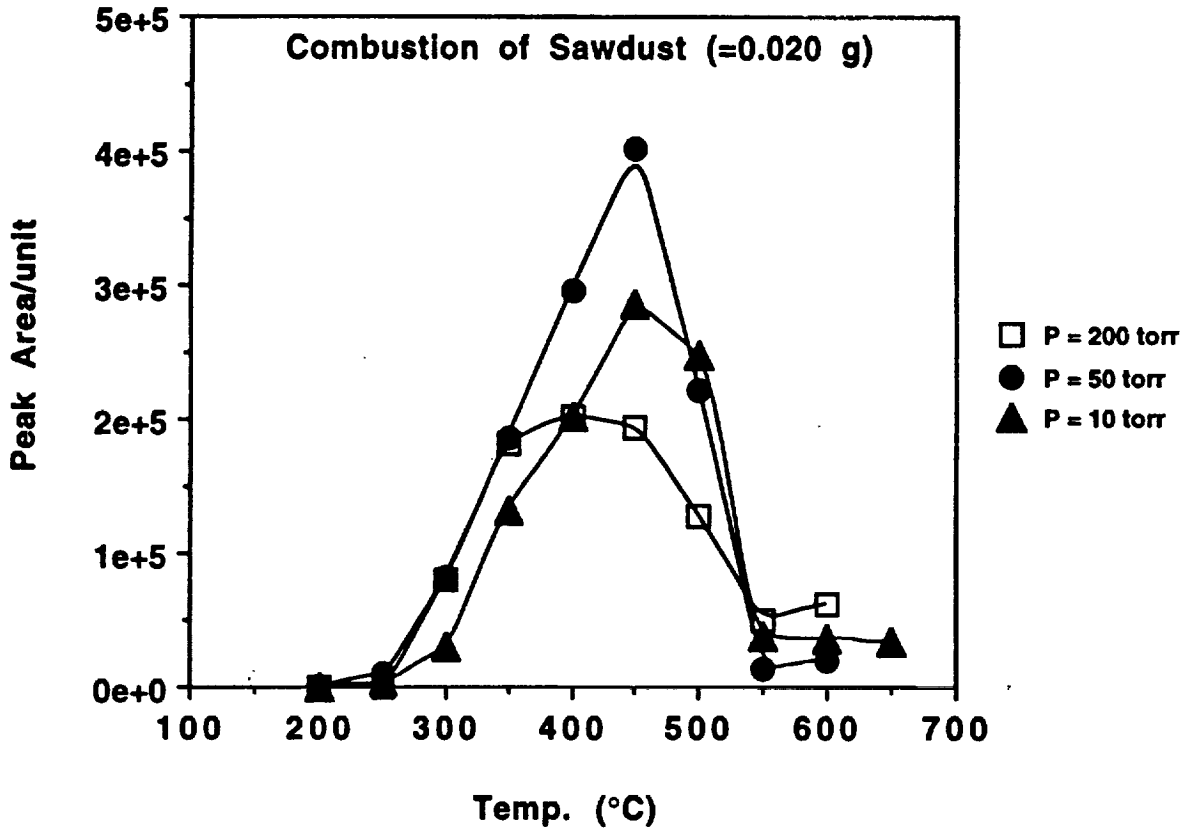

Combustion of Sawdust (=0.020 g)
Peak Area/unit
5e+5
4e+5
3e+5
2e+5
1e+5
0e+0
100
200
300
400
500
600
700
Temp. (°C)
P = 200 torr
P = 50 torr
P = 10 torr

FIG.2

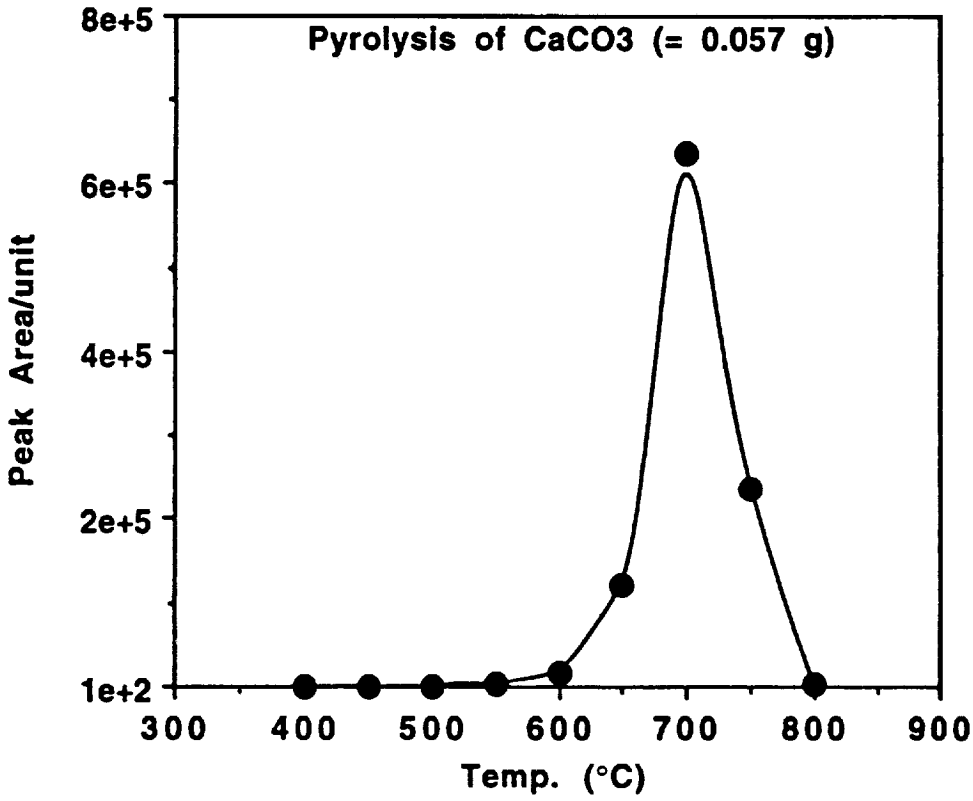
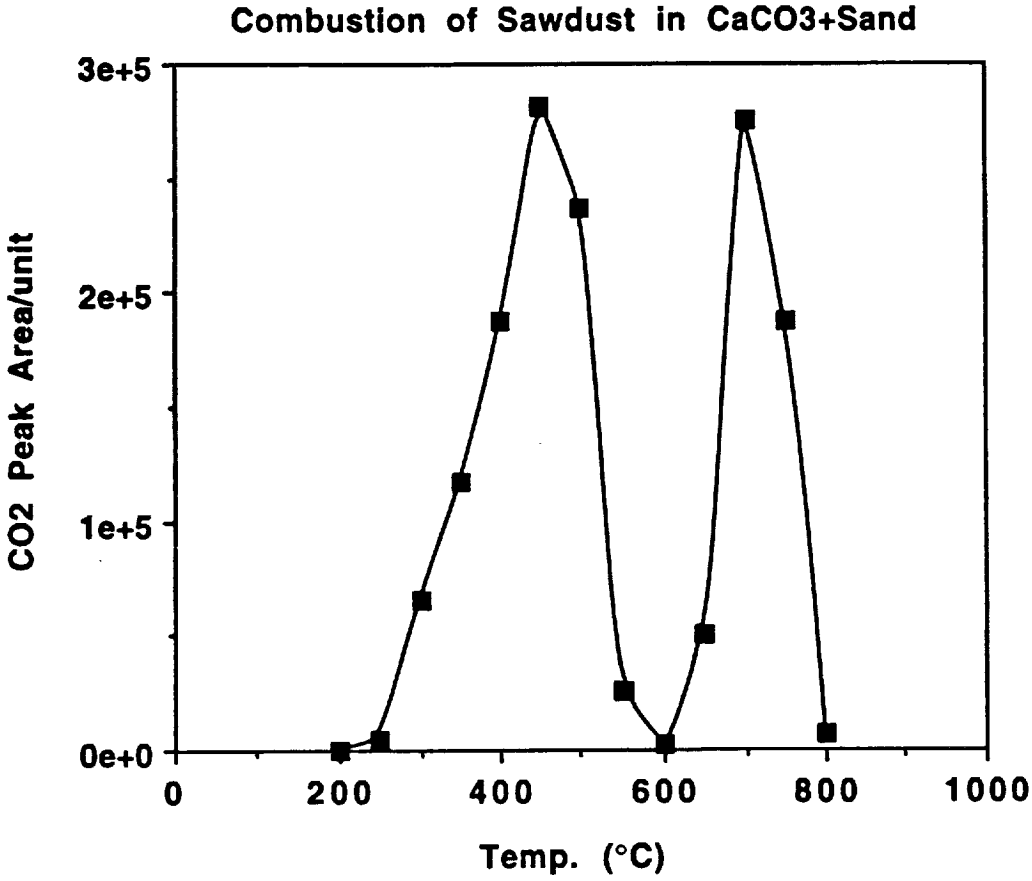

Pyrolysis of CaCO3 (= 0.057 g)
8e+5
6e+5
4e+5
2e+5
1e+2
Peak Area/unit
300
400
500
600
700
800
900
Temp. (°C)

FIG. 3A


Combustion of Sawdust in CaCO3+Sand
CO2 Peak Area/unit
3e+5
2e+5
1e+5
0e+0
0
200
400
600
800
1000
Temp. (°C)

well-separated peaks at 475 and 725 degrees C as expected (shown in Fig. 3). The contribution of Dr. Sam Akapo, an expert in GC techniques and analyses, to the GC pyrolysis experiments is gratefully acknowledged.

We have recently published a report entitled "Stable Isotope Laser Spectrometer for Exploration of Mars" (6) in which we describe an improved Stable Isotope Laser Spectrometer capable of measuring isotopic ratios in carbon, oxygen, and nitrogen. The abstract of this report is reproduced below.

> On Earth, measurements of the ratios of stable carbon isotopes have provided much information about geological and biological processes. For example, fractionation of carbon occurs in biotic processes and the retention of a distinctive 2 to 4 percent contrast in $^{13}C/^{12}C$ between organic carbon and carbonates in rocks as old as 3.8 billion years constitutes some of the firmest evidence for the antiquity of life on the Earth. We have developed a prototype tunable diode laser spectrometer which demonstrates the feasibility of making accurate in situ isotopic ratio measurements on Mars. This miniaturized instrument, with an optical path length of 10 cm, should be capable of making accurate $^{13}C/^{12}C$ and $^{15}N/^{14}N$ measurements. Gas samples for measurement are to be produced by pyrolysis using soil samples as small as 50 milligrams. Measurements of $^{13}C/^{12}C$, $^{18}O/^{16}O$ and $^{15}N/^{14}N$ have been made to a precision of better than 0.1% and various other isotopes are feasible. This laser technique, which relies on the extremely narrow emission linewidth of tunable diode lasers (< 0.001 cm-1) has favorable features in comparison to mass spectrometry, the standard method of accurate isotopic ratio measurement. The miniature instrument could be ready to deploy on the 2001 or other Mars lander missions.
> This work will lead to a better understanding of the requirements necessary to successfully and accurately analyze planetary samples in situ on future NASA exploration missions to Mars.

Two patents (US Patent #5640014, June 6, 1997 and US Patent #5543621, August 6, 1996) "Laser Diode Spectrometer for Analyzing the Ratio of Isotopic Species in a Substance" have been issued. Foreign patents based on these two US patents have been applied for and are expected to be issued. Efforts continue to transfer our NASA-developed technology to a California instrument manufacturer for medical diagnostic breath tests.

PUBLICATIONS and REPORTS

1. "Stable Isotope Ratio Measurements Using Tunable Diode Laser Spectroscopy," J.F. Becker, T.B. Sauke, and M. Loewenstein (1992) Applied Optics, 31, 1921-1927.

2. "An Overview of Tunable Diode Laser Spectroscopy to Stable Isotope Analysis," T.B. Sauke, J.F. Becker, and M. Loewenstein, T.D. Gutierrez, C.G. Bratton (1992) Spectroscopy, 9, 34-40.

3. "Improved Stable Isotope Laser Spectrometer and Its Application to Soil Analysis," T.B. Sauke, J.F. Becker, T.D. Gutierrez, C.G. Bratton in Proc. of Conference on Novel Laser Sources and Applications, (J. Becker, A. Tam, J. Gruber, and L. Lam, eds., SPIE Publ., Bellingham, 1994).

4. Patents #5,543,621 issued August 6, 1996 and #5,640,014 issued June 6, 1997: "Laser Diode Spectrometer for Analyzing the Ratio of Isotopic Species in a Substance."

5. "Thermal Emission Spectra of Mars (5.4 - 10.5 um): Evidence for Sulfates, Carbonates, and Hydrates," Pollack, J. B., Rouch, T., Wittenborn, F., Bregman, J., Wooden, D., Stoker, C., Toon, O. B., Rank, D., and Freedman, R. (1990) J. Geophys. Res. 95, 14595-14627.

6. "Stable Isotope Laser Spectrometer for Exploration of Mars," T.B. Sauke and J.F. Becker (1998) Planetary and Space Sciences, 46, 805-812.